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Fluidities of Thixotropic Gels: Bentonite Suspensions

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Flow measurements on bentonite suspensions, showing both the property of thixotropy and of fluidity variable with shearing stress, were performed in capillary tubes, brass pipes, and a rotary consistometer of special design. The latter instrument was used to show that the structure of such gels must be broken down or built up until an equilibrium state of flow is attained to obtain reproducible measurements. No slippage at the walls was found in non-plug flow. Turbulent flow of bentonite suspensions was investigated in one-half and one-inch pipes. It is demonstrated that these materials behave as any viscous liquid, in the turbulent region, and that the volume of flow at any pressure gradient may be assumed to be the same as for water, without great error. The importance of obtaining equilibrium flow conditions for fluidity measurements is stressed.

I. INTRODUCTION

MANY recent papers, both of research and industrial nature, have considered the flow of fluids that do not have a constant viscosity at constant temperature. Such fluids show the property of an apparent viscosity variable not only with the shearing stress involved, but also with the amount of work that has been done on them. The term "thixotropy" has been applied to those materials which will not only become more fluid as work is done on them, but which, when quiescent, will again lose their fluidity. Bentonite suspensions are familiar examples of such materials. Bulkley and Bitner[1] have shown the breakdown of plastic petroleum oils caused by successive passages through capillary tubes. Such breakdown is also apparent in clays and bentonite suspensions, the measured apparent fluidity increasing with the amount of work done on the material.

The mathematical treatment of the flow of such materials has largely failed to consider this phenomenon. Mooney's[2] and Reiner's[3] equations for slip and fluidity require a condition of equilibrium flow for a substantially homogeneous fluid. The practical difficulty of obtaining an equilibrium state of flow, such that the rate of formation of a thixotropic gel is balanced by its rate of breakdown is difficult to overcome in capillary tubes. The data given herein will attempt to show that, unless such an equilibrium is attained, the measured results are not reproducible and are meaningless for the purpose of flow calculations.

A knowledge of the actual flow characteristics of such fluids is particularly desirable in the petroleum industry, where "gelling" drilling fluids are used for the rotary drilling of oil wells.[4, 5, 6] Papers on this subject do not give an accurate method of predicting the flow of a

[1] Bulkley and Bitner, J. Rheology **1**, 269 (1930).

[2] Mooney, J. Rheology **2**, 210 (1931).

[3] Reiner, J. Rheology **2**, 337 (1931).

[4] Ambrose and Loomis, Physics **1**, 129 (1931).

[5] Farnham, Petroleum Eng. **2**, 5, 117 (1931).

[6] Marsh, Petroleum Development and Technology, A. I. M. E. Transactions, Petroleum Division, p. 234 (1931).

thixotropic clay suspension because "thixotropy" is not considered. No instrument thus far devised has provided data that can be applied to the flow of drilling fluid in actual practice. In the petroleum industry consideration has not been accorded to the fact that drilling fluid may have a turbulent flow region as well as a so-called viscous region. The purpose of the present study has been to investigate the flow of such fluids both in the viscous and in the turbulent regions, with the aim of developing an apparatus suitable for testing and for predicting flow in practice.

The usual capillary viscometer is often employed in determining the consistencies of non-Newtonian fluids. The data of Schofield and Scott Blair[7] on clay suspensions have revealed the variation of rate of shear with tube radius at constant shearing stress. Peek and Erickson,[8] using capillaries of common radius but different lengths, have learned that the apparent viscosities of agar-agar solutions and starch pastes at constant shearing stress are lower in the longer tubes. This finding lends support to the view that the fluidity of such materials is increased by doing work on them. If the measurements could be so made that equilibrium between the breaking down and building up of the gel could be reached, the measurements should be independent of the dimensions of the apparatus. There is no evidence that this is commonly done in a capillary viscometer.

The rotary viscometer of the Couette or Hatschek type enables the treatment of a fluid under substantially constant conditions over a long period of time. A material that exhibits thixotropy may be subjected to a constant maximum rate of shear until the observed torque decreases to a minimum where equilibrium is established between the breaking down and the formation of the gel. Such measurements, made on bentonite-water mixtures, are described below.

Few investigators have extended the study of the flow of pseudo-plastic materials to the turbulent region. Gregory,[9] in a study of the flow of clay slurries in pipes, found that aqueous suspensions, containing as much as 35.3 percent clay by weight, showed in the turbulent region approximately the same flow characteristics as water.

The data given below include measurements of the flow of bentonite suspensions through $\frac{1}{2}$-inch and 1-inch brass pipes. It is shown that the formulae for the turbulent flow of water may be applied to these mixtures with a fair degree of accuracy when the flow is turbulent. True turbulence sets in at higher velocities than for water.

II. Measurements in Capillary Tubes

Rates of flow of bentonite suspensions (5 percent air-dried bentonite by weight) were measured in four capillary tubes of the following dimensions:

Capillary No.	1	2	3	6
Mean radius, R	0.1526 cm	0.1283 cm	0.1091 cm	0.1890 cm
Length	138.1 cm	85.8 cm	91.4 cm	83.5 cm

A rotary gear pump circulated the bentonite suspensions, a portion of which flowed through the capillary, the remainder back to the reservoir. The reservoir was thermostated at 25 ± 0.01°C and thermostat water was circulated through a water jacket around the capillary. The ends of the capillaries were belled into pressure chambers, 1–2 cm in diameter, where connections led to mercury manometers. Efflux was measured in a graduated cylinder. The data are recorded in Fig. 1, where $E/\pi R^3$ is plotted against the shearing stress at the walls of the tube. The symbols are as follows: E = efflux in cm³/sec., R = mean radius of tube, S = shearing stress at wall of tube = $PR/2$, and P = pressure drop (dynes/cm²/cm).

The curves are similar in form to those of Schofield and Scott Blair.[7] According to Mooney's[2] theory, the lack of coincidence of the curves indicates slippage at the walls of the tubes. It is noteworthy that, for these and other data where capillaries of different radii are used, the curves for the larger capillaries always fall lower, indicating a lower apparent fluidity in the larger tubes. But at constant shearing stress a much larger volume per unit time is forced through the larger tube, requiring excess energy to break down its gel structure to the same point as in

[7] Schofield and Scott Blair, J. Phys. Chem. **34**, 248 (1930).

[8] Peek and Erickson, J. Rheology **2**, 351 (1931).

[9] Gregory, Mech. Eng. **49**, 609 (1927).

the smaller tube. For constant shearing stress at the wall, the material flows at higher linear velocity in the larger tube, thus being subjected to the same distribution of shearing stresses for a shorter time than in the small tubes.

The capillary measurements cannot be correlated since they were not made under what may be termed "equilibrium conditions," as explained below. As the fluidity of a bentonite suspension is found to be a function of the shearing stress applied to it, its fluidity varies from a maximum at the wall of a tube to a minimum at $r=0$. As mentioned above, the data of Fig. 1 would indicate slip at the walls according to Mooney's treatment. But Mooney's treatment requires that no factor other than fluidity or slip shall affect the measurements. The fact that the fluidities of such materials are affected by their previous history prevents the application of the Mooney equations unless an equilibrium state of flow is attained.

Capillary measurements present the difficulty of accounting for the energy required to break down the gel structure at the entrance of the tube. A further difficulty in testing clay suspensions, as mentioned by Williamson,[10] is that the particles of clay may be of the same order of magnitude as the diameter of the tube.

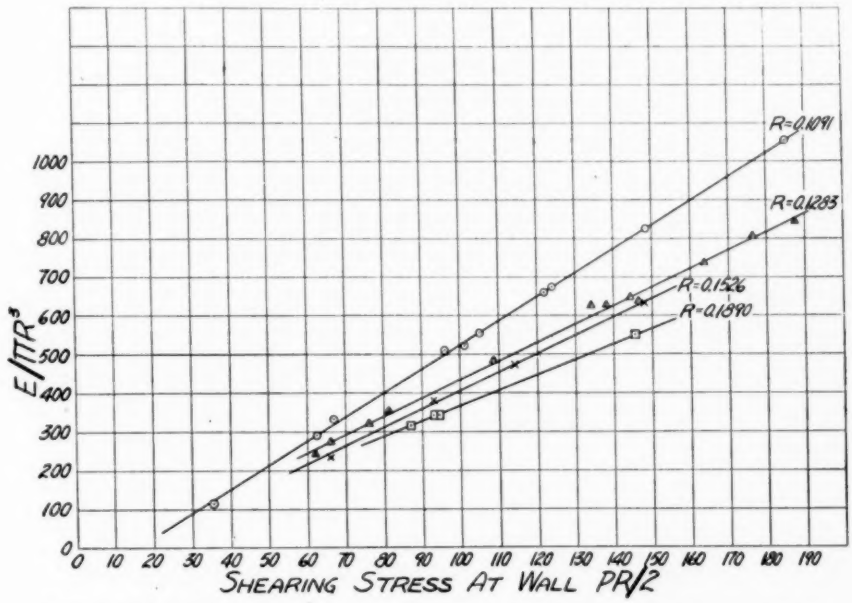

FIG. 1. Flow measurements in capillary tubes. 5 percent bentonite suspension.

III. MEASUREMENTS IN THE ROTARY CONSISTOMETER

The flow characteristics of bentonite suspensions have been further investigated with a rotary consistometer having two inner and two outer cylinders, as suggested by Mooney. The first instrument had a design similar to that described by Hatschek.[11] Since the vertical support rods for the end guards were found to interfere with free motion of the suspended cylinder when a gelling fluid was present, the apparatus was redesigned to eliminate this fault. The newer apparatus has the lower guard plate supported from below by a rod running through a packing gland at the base of the cup. The ends of the inner cylinder are hollowed, allowing an air bubble to be trapped below. The fluid does not touch the under side of the top guard cylinder, nor the under side of the suspended cylinder, thus largely eliminating the causes hindering freedom of motion of the latter. The wire suspension and dial for indicating torque are the same as used on the MacMichael vis-

[10] Williamson, J. Rheology **1**, 283 (1930).

[11] Hatschek, *The Viscosity of Liquids*, p. 53, G. Bell and Sons (1928).

cometer. MacMichael wires were also used, their constants being determined with an oil of known viscosity. Fig. 2 shows constructional features of the consistometer.

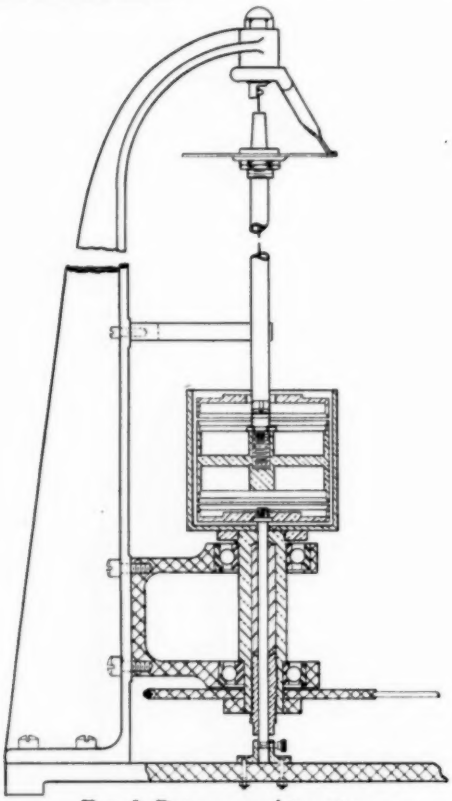

FIG. 2. Rotary consistometer.

The dimensions of the cylinders are given as follows:

		Radius	*Length*	*Description*
a	Outer cylinder	4.674 cm		Cup
b	Inner cylinder	4.420	5.40 cm	Cylinder
b	Outer cylinder	4.420		Cup
c	Inner cylinder	4.166	5.40	Cylinder

The length of the outer cylinders is immaterial to the calculations.

It is evident that three combinations of radii, *ab*, *bc*, and *ac*, may be used. These combinations allow the determination of slippage at the wall, as shown by Mooney. The outer cylinder may be revolved at various constant speeds, the resulting moment on the inner cylinder being measured in degrees deflection of the torsion wire.

1. Equilibrium measurements

Fig. 3 shows the variation of measured torque with rate of revolution of the outer cylinder for a 5 percent suspension of bentonite. The measurements were made at successive constant rates of revolution, the arrows indicating the direction in which the r.p.s. was changed for successive measurements. Torque is measured in MacMichael degrees (300°M = 360°). The curves plainly show that the fluidity of the material at constant r.p.s. is dependent upon its previous history. At constant r.p.s. the fluidity is increased by subjecting the fluid for a short time to a higher r.p.s.

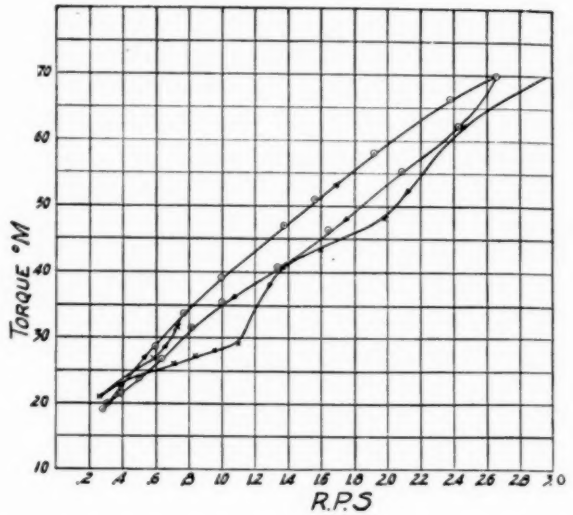

FIG. 3. Variation of fluidity with treatment. 5 percent bentonite suspension.

It was found that a substantially constant deflection could be attained by subjecting the fluid to constant angular velocity for a period of 30 minutes to several hours. The period necessary to break down the gel until equilibrium between angular velocity and shearing stress was reached was shorter than that of reformation of a gel that had been subjected to high velocity. Therefore successive measurements were made at increased velocities.

Fig. 4 illustrates variation of measured torque with time for a 5 percent bentonite suspension at several constant velocities. At 3.68 r.p.s. the increase in apparent fluidity amounted to more than 16 percent in 50 minutes. The value °M = 66.0 for zero time is smaller than the actual initial deflection; the initial decrease in torque during the first few seconds is very large.

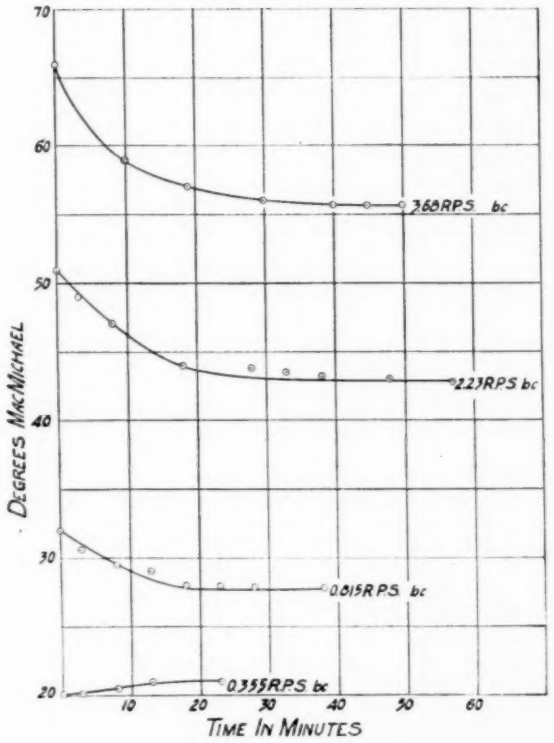

FIG. 4. Variation of torque with time at constant rate of rotation. 5 percent bentonite in rotary consistometer.

2. Slip

To determine if slippage occurs at the walls for a 5 percent bentonite suspension, measurements were made with the three combinations of radii *ab*, *bc*, and *ac*. The results, plotted in Fig. 5, measured at 25.5±0.5°C, required four days time, and include check runs on each combination of cylinders. The apparatus was operated in a constant temperature room, but control of temperature to better than ±0.5°C was difficult. Previous work had shown that the effect of moderate temperature changes on the apparent fluidities of such fluids is small.

According to Mooney's theory, slippage occurs if

$$\Omega ab + \Omega bc > \Omega ac,$$

where Ω = angular velocity at constant applied torque T. For this instrument,

$$T = 1.2N°\mathrm{M}/L,$$

where the factor 1.2 converts MacMichael degrees to circular degrees, N = restoring moment of the wire and L = length of inner cylinder.

Since T is directly proportional to °M and Ω to r.p.s., the measured units may be plotted directly. The dotted curve *ac* in Fig. 5 represents the sum of the value of *ab* and *bc* for constant torque. The results do not show evidence of slippage.

The same data are further shown in Fig. 6, a log *vs.* log plot of rate of shear $\Omega/\epsilon = S\phi$ against average shearing stress S. The symbols are those used by Mooney:

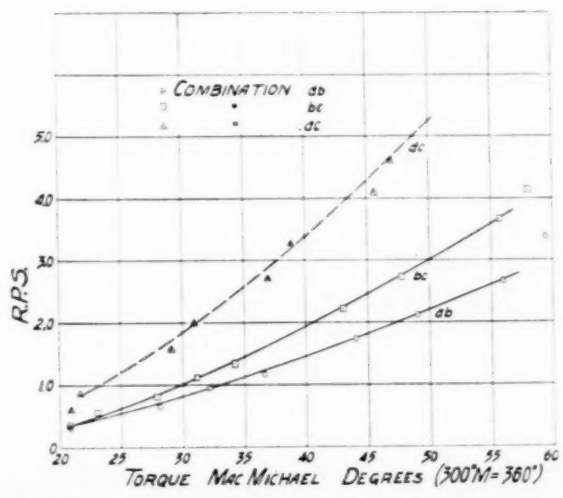

FIG. 5. Flow measurement with rotary consistometer. 5 percent bentonite suspension.

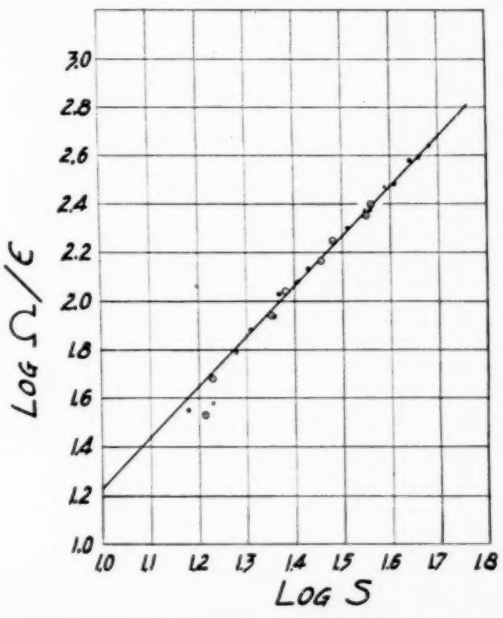

FIG. 6. Rotary consistometer-rate of shear *vs.* shearing stress. 5 percent bentonite suspension.

Ω = angular velocity of outer cylinder,
$\epsilon = (R_2^2 - R_1^2)/(R_2^2 + R_1^2)$,
R_1, R_2 = radius of inner, outer cylinder,
$S = (S_1 + S_2)/2$ average shearing stress,
$\phi = (1/s)r(d\omega/dr)$,
r = distance from common axis of the cylinders,
s = shearing stress at r, and
ω = angular velocity of fluid at r.

In the absence of slippage, Mooney's Eq. (30) for fluidity at the average shearing stress between the two cylinders should hold:

$$S\phi \doteq \Omega/\epsilon.$$

Excepting the three lowest points in Fig. 6 it is found that the data represent a substantially straight line. Then:

$$\Omega/\epsilon = mS^n = S\phi, \quad \text{and} \quad \phi = mS^{n-1}.$$

By substitution in the equation for tube flow, $dv/dr = s\phi$ we obtain $dv/dr = ms^n$.

By integration and substitution of v in

$$E = 2\pi \int_0^R vrdr,$$

an equation is obtained for flow in tubes:

$$E/\pi R^3 = mS^n/(n+3),$$

This equation is intended to represent flow in a tube where equilibrium has been attained in the breakdown and reformation of a gel. Such a condition is difficult to picture in a tube because of the wide range of shearing stresses from 0 to $PR/2$. If the material does not attain equilibrium in the rotary consistometer for 30 minutes, it would hardly be possible to reach equilibrium in a capillary of a length usually employed for viscosity measurements.

The failure in agreement between measurements in tubes and in the rotary instrument is shown in Fig. 7, where curve A represents the values of $E/\pi R^3$ as a function of shearing stress at the walls, as calculated from the above equation.

If the data are correctly analyzed, there is no slippage at the walls in non-plug flow and the fluidity of fluids of this type may be represented by the equation

$$\phi = ms^{n-1}.$$

But this equation only holds when the gel has been broken down by subjecting it to the same mechanical treatment over a protracted time. This being true, the fluidities cannot be applied to flow through tubes in which the time factor is unknown.

To determine further whether or not the relationship between fluidity and shearing stress just given is correct, several other concentrations of bentonite were investigated, using a single combination of radii $-ac$.

The results are shown in Fig. 8, where the log of the rate of shear Ω/ϵ is plotted as a function of the log of average shearing stress S. There are shown the curves for water as well as an oil used in calibrating the torsion wires. According to the data of Mallock,[12] the critical angular velocity for the revolving cylinder of a rotary viscometer is:

$$\Omega_c = 1900\eta/(R_2^2 - R_1R_2)d,$$

where 1900 is the Reynolds number, η = viscosity, and d = density of fluid. The critical value of Ω_c/ϵ for water at 25°C is calculated to be

$$\Omega_c/\epsilon = 62.4.$$

It will be noted that the curves for 2.4 and 3.0 percent bentonite show a break in the neighborhood of this value. It is possible that turbulence of a portion of the water above a certain critical value causes a sudden increase in apparent fluidity. The curves for both the 2.0 percent and 4.4 percent suspensions show a departure from linearity at velocities considerably higher than the critical velocity for water. It is clear that a single equation cannot be used to represent the flow of these suspensions in the rotary instrument throughout their region of so-called viscous flow.

IV. Measurement in Brass Pipes

Flow measurements of bentonite suspensions were further extended to a large scale flow apparatus having ½-inch and 1-inch brass pipes. A rotary gear pump forced the fluid through pipe coils having a radius of curvature of about 5 ft. Volumes were measured in gallons, indicated by the change in level of a float in a steel drum. Pressures were measured by a differential mer-

[12] Mallock, Phil. Trans. **A187**, 41 (1896).

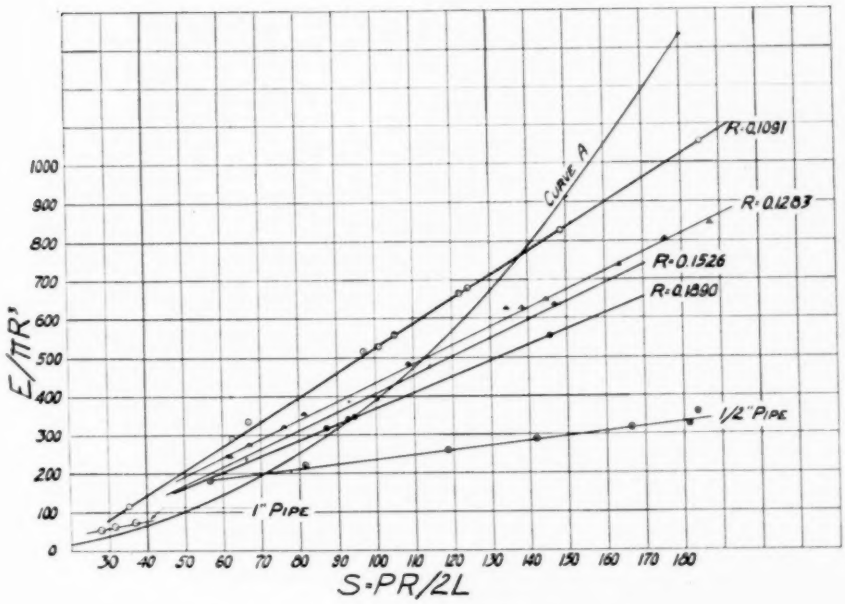

FIG. 7. Flow of 5 percent bentonite suspensions.

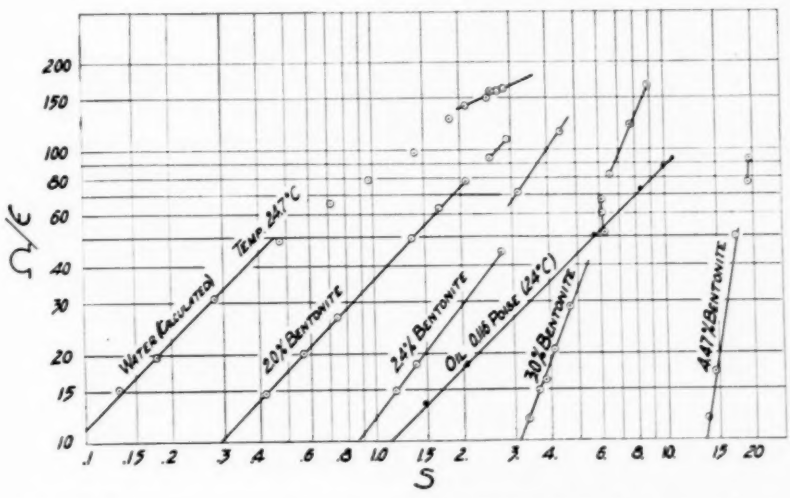

FIG. 8. Flow measurements in rotary consistometer. Bentonite suspensions.

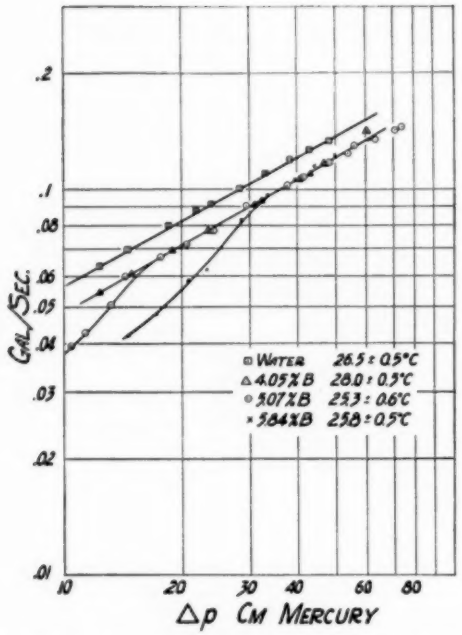

FIG. 9. Flow of bentonite suspensions in ½-inch brass pipe.

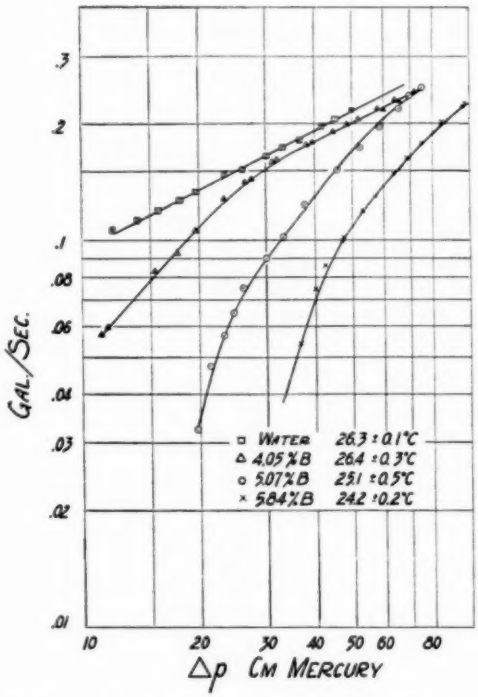

FIG. 10. Flow of bentonite suspensions in 1-inch brass pipe.

cury manometer whose leads were connected to pressure taps in the pipes. Dimensions are given as follows.

Inside radius	*Distance between pressure taps*
0.635 cm	442. cm
1.270	5385.

The data for several bentonite suspensions are shown in Fig. 9 and Fig. 10, where log (gal./sec.) is shown as a function of log (total pressure drop) in centimeters of mercury. There is no end correction for the pressure drop because the taps were some distance from the ends of the pipes. The experimental points for water are included in the data.

It is notable that the data for three concentrations of bentonite all fall on the same line in the turbulent region (Fig. 9), and that this line is substantially parallel to that for water. The effective fluidities of the several concentrations are the same in the turbulent region, but the critical velocity is higher the higher the concentration. It is evident that for pipes ½-inch or more in diameter, flow of these and similar fluids in the turbulent region may be assumed to be approximately the same as that of water for engineering calculations. The experiments of Gregory support this view. The difficulty still exists that the critical velocity is not known for such materials and would have to be determined experimentally for any fluid. The data for nonturbulent flow of the 5.07 percent bentonite are also plotted in Fig. 7 for comparison with the capillary tubes.

V. CONCLUSIONS

Flow measurements were made on bentonite suspensions, which show to a marked degree both the properties of thixotropy and of fluidity variable with the shearing stresses applied to them. Such liquids are fairly reproducible, and are similar in properties to clay suspensions and fluids used in the rotary drilling of oil wells.

Flow measurements in capillary tubes were not considered to give data applicable to flow in any other apparatus because the degree of gel of fluids showing marked thixotropy cannot be reproduced with certainty except under conditions of long-time flow. Capillary measurements of flow of clay suspensions and similar materials present the further difficulty that the suspended particles are often of the same order of magnitude as the diameters of the tubes. This condition

prevents a simple, accurate mathematical analysis of the flow of such fluids.

Measurements of the flow of bentonite suspensions in a rotary consistometer indicate that, in non-plug flow, there is no slippage at the walls of the cylinders. The fluidity of such fluids may be considered as a function of the shearing stress to which it is submitted:

$$\phi = ms^{n-1}.$$

Lower concentrations of bentonite showed a departure from linearity of the log (Rate of Shear) *vs.* log (Average Shearing Stress) relationship at about the critical angular velocity for water in this instrument.

Experiments on the flow of bentonite suspensions in pipes showed that these materials behave as any viscous liquid in the turbulent region, and that the volume of flow at any pressure gradient may be assumed to be the same as that for water, without great error. The agreement will be better the greater the pipe diameter.

This paper is intended to emphasize some of the difficulties encountered in investigating the flow of clay suspensions and similar fluids, without presenting any definite way of predicting flow under all conditions. The problem is still an open one. It is believed that the time factor has often been neglected in considering the flow of nonviscous materials. It is evidently important to subject such fluids to the same mechanical treatment before a true knowledge of their properties may be known.

Acknowledgment

It is a pleasure to acknowledge the helpful advice and criticism of Dr. P. D. Foote and Mr. R. J. S. Pigott of the Gulf Research and Development Corporation during the preparation of this paper.

Progress Report on the Determination of Absolute Viscosity*

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(Received May 4, 1933)

An apparatus designed for the precise measurement of absolute viscosity is described. The liquid being studied is caused to flow from one reservoir through a capillary tube into a second reservoir, the pressure difference between the two being measured with a differential manometer. Various rates of flow are caused by injection of mercury into the upstream reservoir from a cylinder by means of a uniform piston driven at constant speed by a synchronous motor through a gear train. A number of interchangeable capillaries of different bore diameters and lengths can be employed. The displacement apparatus and the viscometer are thermostated in baths designed for precise temperature control. A machine designed and built to lap the bores of capillaries into right circular cylinders is described.

Introduction

With the cooperation of the Society of Rheology and the Chemical Foundation,[1] an investigation of the absolute viscosity of water at various temperatures was undertaken by the Bureau of Standards. To this end an apparatus has been designed for studying the flow of liquids through capillary tubes under conditions so precisely controlled as to permit accurate experimental evaluation of boundary effects. With this apparatus it is hoped that it will be possible to determine directly, in terms of the fundamental definition, the absolute viscosity, not only of water but of other liquids covering a wide range of viscosities, with attendant uncertainties several times smaller than the existing ones for water, which amount to at least 0.2 percent,[2] and possibly ten to one hundred times smaller than those for liquids of high viscosity. The establishment of a number of liquids as secondary reference standards would be of great assistance in increasing the accuracy of measurements made with relative viscometers.

As the rate of flow of a liquid through a cylindrical capillary approaches zero and as the tube approaches infinite length, the viscosity η as computed by Poiseuille's formula:

$$\eta = \pi r^4 p / 8lq$$

approaches the true viscosity. In the above equation r is the radius and l the length of the capillary, p is the pressure difference between the ends, and q is the rate of flow through the capillary. If the quantities on the right of the equality sign are expressed in c.g.s. units, the unit of viscosity is one poise. When the liquid is forced at a finite rate through even a perfect capillary tube of finite length, the phenomenon which occurs is complicated by extraneous effects, not covered by the above equation, which necessitate the application of corrections before the true viscosity can be calculated.

Various theoretical derivations have been made of the form which these correction terms should take, but the solution of the general problem is not simple from a hydrodynamic standpoint and data at present available are insufficient to make a thorough test of the general validity of the theoretical derivation. From this lack arises much of the uncertainty in the present values of absolute viscosity.

An experimental evaluation of end effects is possible by making a series of runs in which the rate of flow and length of capillary are varied, and by extrapolating to zero rate of flow for a tube of infinite length. Any effect of magnitude of radius on the applicability of Poiseuille's law should be discoverable by a comparison of the results obtained from a number of tubes of different radii.

* Publication approved by the Acting Director, Bureau of Standards, U. S. Department of Commerce.

[1] Acknowledgment is made to the Chemical Foundation for their financial support of this project up to February 1, 1933. Since that time the work has been continued under a temporary plan, but may have to be suspended indefinitely before conclusive results have been obtained.

[2] Int. Crit. Tab. **5**, 10 (1929).

A treatment such as that outlined above is greatly simplified if the capillary tubes closely approximate right circular cylinders and if tubes of various lengths can be prepared with the same size of bore. For this reason, particular emphasis has been placed on the preparation of suitable capillary tubes. Precision in the evaluation of the end effects has been sought by a reversal of the customary technique for absolute viscosity measurements, as described later.

The Capillary Tubes

While it is true that the simple Poiseuille law can be modified to apply with undiminished rigor to tubes whose bores are right elliptical cylinders, and with a high order of approximation to tubes whose bores are uniform conic segments, the use of noncylindrical tubes would greatly complicate the procedure of evaluating end effects. For this reason it was decided to obtain, if possible, tubes which could be regarded as right circular cylinders without introducing an error in the measured viscosity greater than that permitted by the general accuracy obtainable. From the expressions used by Knibbs[3] for the flow through elliptical and conical tubes it is easily calculable that an ellipticity so great that the difference between the major and minor semi-axes amounts to 2 percent of the mean radius will introduce an uncertainty in the viscosity of only 1 part in 10,000, and a conicality so great that the difference between the radii at the two ends amounts to 1 percent of the mean radius will introduce an uncertainty of less than 1 part in 10,000.

The limits of tolerance for deviations in the capillary bores having been thus determined, it remained to decide how best to obtain such tubes. Three methods were considered: first, to select such tubes by examination from a great number of tubes commercially available; second, to have tubes especially made for the purpose by some process such as drawing them down in vacuum on a lapped wire, the wire being subsequently removed by acid; and third, by starting with a reasonably good tube chosen from stock and improving the bore by lapping until it meets requirements. The first two methods were discarded because of the time required to carry out the first and the technical difficulties involved in the second.

Based on the third method, a machine has been constructed which tends to reshape the bores of capillary tubes into circular cylinders by a lapping process. The tube is mounted vertically in a frame which slowly oscillates about its vertical axis with an amplitude of unequal magnitude in the two directions so that a resultant slow rotation occurs such that the tube comes to rest at any one point only once in a great number of revolutions. The lapp is carried on a wire which is automatically drawn up and down through the tube. The method of mounting the tube in the machine is shown in detail in Fig. 1. An aluminum collar is clamped on the tube toward each end and these are attached to the oscillating frame by vertical springs so that for small lateral displacements the force tending to restore the tube to its equilibrium position is very small. This facilitates alignment of the axes of wire and frame, greatly reduces the evils of misalignment, and makes it possible with reasonable care to remove the tube from the machine for examination and subsequently to return it for further work with-

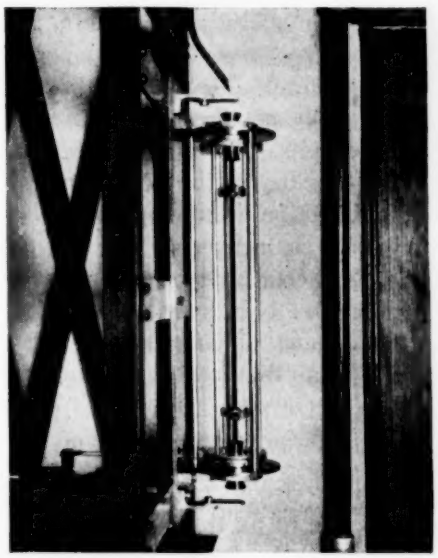

Fig. 1. Method of mounting capillary tube in lapping machine. The capillary tube is shown in black for greater contrast.

[3] Knibbs, Roy. Soc. of New South Wales **29**, 77 (1895); **30**, 190 (1895).

out resort to elaborate centering devices. Preliminary experiments have indicated a marked improvement in the capillary bore, and further work is under way to increase the efficiency of the lapping process.

The examination of the tube has been divided into three parts: first, a direct observation of the bore diameter with a low power microscope to determine the straightness and approximate size of the bore; second, a direct observation of the bore diameter by means of a high power microscope (50 diam.) to determine the amount of ellipticity and conicality present; and finally, a determination of the mean diameter by a mercury thread calibration. For the direct measurements of the diameter, the tube is thoroughly cleaned, evacuated, and filled with mercury; placed in a glass-bottomed tank containing an oil mixture having the same index of refraction as the glass; and illuminated from below with filtered, monochromatic light from a mercury arc lamp. Measurements are made with a microscope fitted with a calibrated filar micrometer eyepiece. The accuracy obtainable is somewhat better than 0.0005 mm, which permits the detection of much smaller variations in bore diameter than those which are apparently permissible. No accurate determinations of mean diameter have yet been made, but weighing of a measured length of mercury thread as an indication of mean diameter is contemplated.

The Viscometer

In most tube viscometry in the past it has been the practice to fix the pressure causing the flow and measure the time required for a given volume of fluid to flow through the capillary. This method introduces difficulties due to imperfect drainage, errors in time measurement, and change in the pressure head during the course of a run. To avoid these difficulties it was decided to predetermine the rate of flow through the capillary and to measure the resultant pressure difference between the two ends. The type of viscometer adopted is shown in a very much simplified form in the diagram of Fig. 2. The piston *A* is driven at a constant rate into the cylinder *B* forcing mercury over into the upstream reservoir *C* from whence the

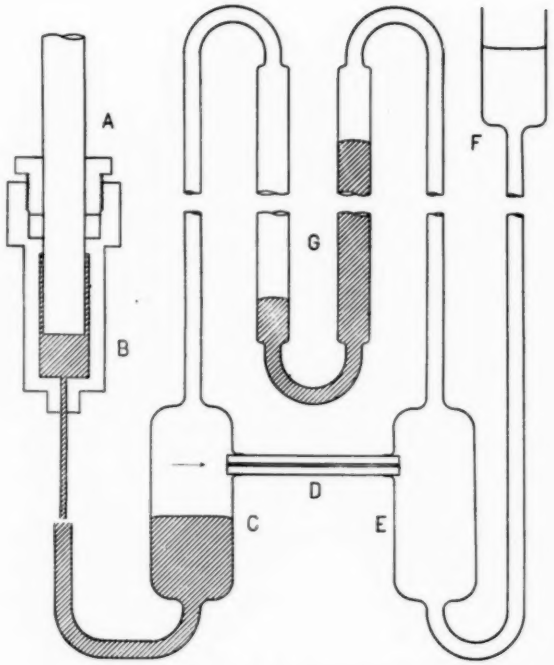

Fig. 2. Schematic diagram of viscometer.

liquid whose viscosity is to be measured is forced through the capillary *D* into the downstream reservoir *E* and finally up into the overflow reservoir *F*. When the system has come to equilibrium the pressure difference between the two reservoirs is measured by the differential manometer *G*.

The assembled displacement mechanism is shown in Fig. 3, the thermostat bath and housing having been removed. The mercury is contained in a steel cylinder from which it is forced by a piston entering through a suitable packing. The piston is rigidly coupled at its upper end to a screw which is moved up and down by a rotating nut, the latter having cut on its periphery worm gear teeth which mesh with a worm on the driving shaft. The screw is prevented from turning by means of a yoke on its upper end fitted with ball-bearing rollers which travel on ground vertical guiding surfaces. This mechanism is driven through a gear box by a synchronous motor operating on a circuit in which the frequency is held accurately constant at 60 cycles by a device which removes second order fluctuations in the controlled frequency power network.

The precision with which the rate of flow is

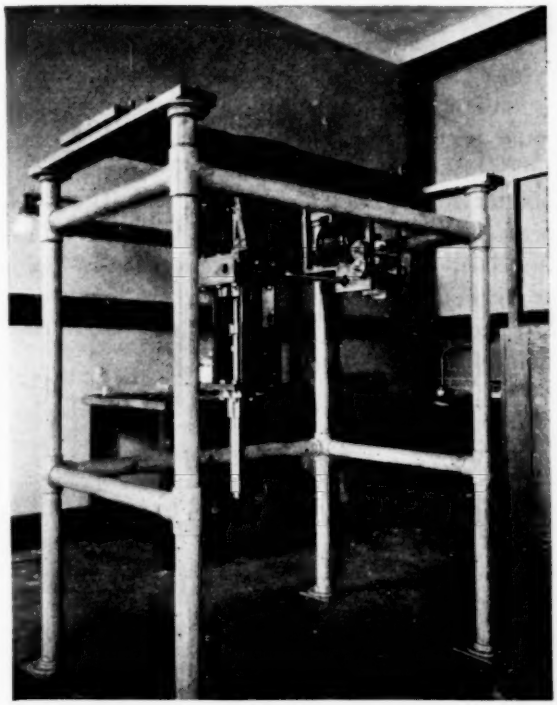

FIG. 3. Assembled displacement mechanism with thermostat bath removed.

known depends on the uniformity of diameter of the piston and the uniformity of the rate at which it advances. The piston is made of a special oil-hardening, nondeforming steel, hardened, ground, and lapped. It is approximately 1 inch in diameter and 10 inches long, and is uniformly circular throughout its length within a tolerance of 0.0001 inch. The screw and worm-gear were made for the purpose, as a unit, through the cooperation of the Hanson-Whitney Machine Company of Hartford, Connecticut, and the screw is guaranteed to have no periodic error greater than 1 part in 10,000. Accordingly, the rate of volume displacement of the piston should be constant to 0.01 percent. Different constant rates of displacement are obtainable by changing sets of gears in the gear box.

The piston and cylinder are immersed in a thermostat oil-bath, the temperature of which can be kept constant to ± 0.001°C. If this part of the viscometer is held at the same temperature during all experiments, it is necessary to introduce a temperature equalizer between the displacement apparatus and the viscometer proper. For this purpose, the mercury from the injector is led by means of steel tubing into a coil, located in an intermediate bath, designed to bring the mercury temperature to within 0.01° of the final value. The mercury is finally conducted into the up-stream reservoir of the viscometer which is located in a third thermostat bath, the temperature of which can be controlled within ± 0.001° at any point from 0 to 100°C.

With the above apparatus, the liquid under investigation is forced through the capillary at a rate which it is believed will be determinable to within 1 part in 10,000. Small variations in the rate of flow are of importance only insofar as they may be the cause of fluctuations in the manometer levels of such magnitude that the latter cannot be read with sufficient precision. Preliminary evidence indicates, however, that any fluctuations will be less than 0.01 mm of mercury.

The design of the manometer is based on the use of a potentiometric method of determining the pressure difference between the two end reservoirs. By means of an injector, the mercury levels in the two arms of the manometer can be pre-set so that their difference in height corresponds approximately to the pressure expected for any given run. After the flow is started a valve between the two arms of the manometer is opened and the level in the upstream arm is held at a fixed position by means of a small mercury injector until no further tendency for it to change can be observed. The second injector is not shown in Fig. 2.

It can be shown by a mathematical analysis of the system that if the manometer levels are pre-set and if the pressure difference shows no tendency to change over a period of several minutes, the difference in height in the two arms corresponds precisely with the rate of flow into the reservoir, which must equal the rate of flow through the capillary. It can be further shown that the slight pressure fluctuations due to variations in the rate at which mercury enters the reservoir from the displacement mechanism are effectively damped out by the manometer. The amount of damping exerted and the time required for the attainment of equilibrium increase as the diameter of the manometer arms increases.

While the assembly of the final viscometer, equipped for interchangeable capillaries, has not yet been completed, preliminary experiments have been satisfactory.

Conclusions

The apparatus which has been developed primarily for the measurement of the absolute viscosity of water is capable of many applications. Thus, it should be possible with equal facility to measure the absolute viscosity of any truly viscous liquid and thereby set up a number of secondary viscosity standards. The availability of these standards would avoid the necessity of any stepping-up process in calibrating a viscometer for liquids of high viscosity, and would permit the calibration with two or more liquids covering the range of the relative viscometer so as to evaluate more accurately any corrections for boundary effects. One of the most important applications of the apparatus lies in the evaluation of end effects over a wide range of viscosities and in investigating deviations arising from nonlaminar flow.

Viscous Resistance in Capillaries of Non-Uniform Radius

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(Received December 14, 1932)

The viscous resistance offered by a tube of varying radius to the flow of a liquid is discussed. Three cases are taken up, for which solutions assume the forms:

(1) capillary tube viscometer:

$$\eta = \pi P / 8 Q A_L.$$

(2) Bingham and Murray plastometer:

$$\eta = P(t - t_1)/8[f_3(l) - f_3(l_1)].$$

(3) apparatus for studies of wetting under dynamic conditions:

$$\gamma = 4\eta f_5(l)/t.$$

The functions A_L, $f_3(l)$, and $f_5(l)$, may be obtained from a calibration of the tube, use being made of graphical integration.

Introduction

IN connection with the development of a method for studying the wetting of solids by liquids, a procedure for graphical calculation of the viscous resistance in a tube of non-uniform radius has been evolved. Other authors[1] have applied similar methods to the ordinary capillary tube viscometers, but an extension to other instruments does not appear to have been made. The application to two types of viscometers and to measurements of wetting is discussed below.

Viscous Resistance in a Tube of Uniform Radius

Calculation of the resistance offered to the flow of a viscous liquid in a capillary tube is readily carried out when the tube has a cylindrical bore of uniform cross section.

Poiseuille's Law states that the rate of efflux, Q, from a tube of radius R and length L is given by the equation

$$Q = P\pi R^4 / 8\eta L, \tag{1}$$

where P is the pressure effective in moving the liquid and η is the viscosity of the liquid.

For convenience, this may be written in the form:

$$Q = P/\omega, \tag{2}$$

where ω, the viscous resistance, is given by the equation

$$\omega = 8\eta L / \pi R^4. \tag{3}$$

Hence for a tube of known uniform radius, the resistance offered to flow may be calculated directly from Eq. (3). The assumption of a tube of uniform bore has often been made in calculating viscosities. Since the resistance varies inversely as the fourth power of the radius, it is obviously necessary for absolute measurements that R actually be uniform within narrow limits to justify such an assumption, or that the true effective value of R be determined by some method of graphical analysis.

Viscous Resistance in a Tube of Non-Uniform Radius

Unfortunately, it usually happens that uniformity is difficult to obtain. Especially is this true where a comparatively long piece of tubing is required as in the Bingham and Murray[2] plastometer or in the measurement of wetting by the dynamic method referred to above and described below in detail. Furthermore, a number of practical problems arise in which the treatment requires the recognition of a variation in pore size from point to point. In this connection may be mentioned, for example, the rise of liquids in sands, and the penetration of liquids into fibrous materials, as in impregnation processes.

[1] See for example, Barr, *Monograph of Viscometry*, p. 60 (1931).

[2] Bingham and Murray, Proc. A. S. T. M. II, **23**, 655 (1923).

In the case of capillary tube instruments, it usually happens that a tube picked at random is sufficiently uniform for the assumption of laminar flow at each cross section. (For the limits within which this is true the reader is referred to the discussion by Bond.[3]) It will frequently be found convenient to be able to calculate the resistance to flow offered by such a tube. For this, it is necessary to have a knowledge of the radius of the tube at each place along its length, which may be found by the usual method of calibration with a mercury thread. Needless to say, the most reliable set of data is obtained by using a comparatively short thread of mercury and measuring its length at a large number of places. This discussion takes no account of ellipticity of bore, and hence the ends of the tube should be examined to make sure that the bore is cylindrical.

The application of a method involving a graphical calculation of viscous resistance to three types of capillary tube instruments is discussed below. The cases chosen to illustrate the method are: (1) the capillary tube type of viscometer; (2) the Bingham and Murray plastometer; (3) apparatus for studies of wetting under dynamic conditions.

The Capillary Tube Viscometer

The simplest case to be considered, in which it is desired to know the viscous resistance occurring in a capillary of non-uniform radius when it is completely filled with the flowing liquid, is exemplified in the Ostwald or Bingham types of viscometers. As indicated above, the radius, R, is known as a function of the distance, l, from one end of the tube. Such information

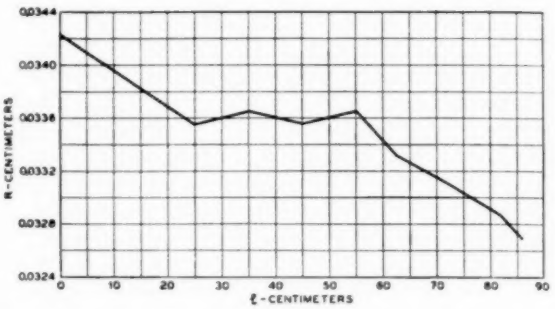

FIG. 1. Plot of R as a function of the distance from one end of tube.

may be represented by a plot such as Fig. 1, which is made from an actual set of data. It is not, however, presented as an ideal set of data, since the radius was determined only at 10 centimeter intervals.

We may consider the tube to be made up of a series of short capillaries placed end to end. Their lengths will be designated by δl_1, δl_2, δl_3, etc., and their respective radii will be called R_1, R_2, R_3, etc. The viscous resistance of the whole tube of length L will be the sum of the resistances of the short tubes taken separately. This may be shown as follows:

The total pressure drop along the tube is equal to the sum of the pressure drops in the short capillaries. That is,

$$P=(P_1+P_2+P_3+\cdots)=Q\omega.$$

But

$$P_1=\frac{8\eta Q}{\pi}\frac{\delta l_1}{R_1^4}, \quad P_2=\frac{8\eta Q}{\pi}\frac{\delta l_2}{R_2^4}, \quad \text{etc.}$$

Substituting these values in the above equation, we obtain*

$$\omega=\frac{8\eta}{\pi}\left(\frac{\delta l_1}{R_1^4}+\frac{\delta l_2}{R_2^4}+\frac{\delta l_3}{R_3^4}+\cdots\right). \qquad (3a)$$

[3] Bond, Proc. Phys. Soc. **34**, 25 (1921).

* Eqs. (2) to (3a) may be recognized as examples of the hydraulic analogy of electrical circuits. Eq. (2) may be likened to Ohm's law in electrical theory in which $I=(E/Z)$. Q, the rate of flow of liquid, is analogous to I, the rate of flow of electricity, and P corresponds to the electrical pressure E. ω may be likened to Z, the electrical resistance of the conductor. The value of Z for a cylindrical conductor is equal to $\rho L/\pi R^2$ where ρ is the specific resistance of the conductor material. Likewise, in Eq. (3), ω is given by $8\eta L/\pi R^4$. Hence, η corresponds to ρ. The factor dependent upon the dimensions of the conductor is $8L/\pi R^4$ in viscous flow and $L/\pi R^2$ in electrical theory. This difference arises from the fact that in the case of a liquid flowing in a tube there is a variation in velocity from zero at the wall to a maximum in the center, while in electrical theory, uniform conduction is assumed. In Eq. (3a), it is shown that viscous resistance in tubes in series connection may be added just as can electrical resistances (provided there are no abrupt changes in cross section). It can easily be shown that in parallel connection viscous resistances obey the same laws as electrical resistances.

If the increments of length be taken very small,

$$\omega = \frac{8\eta}{\pi} \int_0^L \frac{1}{R^4} dl. \tag{4}$$

Now on another graph (Fig. 2) we may represent a function of l, $1/R^4$, which we shall call $f_1(l)$.

Then

$$\omega = \frac{8\eta}{\pi} \int_0^l f_1(l) dl. \tag{5}$$

But this integral is equal to the area $ABCD$ (Fig. 2). This area, A_L, may be obtained by

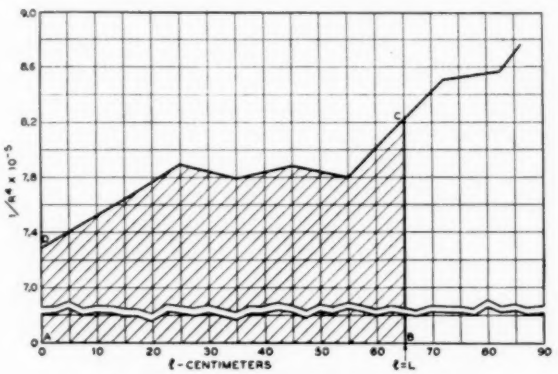

FIG. 2. $1/R^4$ as a function of l, $f_1(l)$.

counting squares or by a planimeter, and we may now write

$$\omega = 8\eta A_L/\pi. \tag{6}$$

This is substituted back into Eq. (2) with the result,

$$Q = \pi P/8\eta A_L. \tag{7}$$

For a given test with the instrument, with P being held constant, η can be calculated:

$$\eta = \pi P/8QA_L = CP/Q, \tag{8}$$

where $C = \pi/8A_L$, a constant of the instrument.

THE BINGHAM AND MURRAY PLASTOMETER

The Bingham and Murray plastometer is not always used under conditions where variations in capillary radius need be taken into account. However, when such is the case, absolute measurements will not usually be made, but calibration with a liquid of known viscosity will be resorted to.

The procedure of graphical calculation for the Bingham and Murray plastometer is slightly more complex than the problem treated above. In this instrument the liquid whose viscosity is to be determined is forced into a capillary tube by a constant pressure. The time is taken at which the advancing meniscus reaches various graduated marks along the tube. The amount of the tube filled and hence the viscous resistance varies from time to time during the run.*

It is now necessary to make use of Eq. (2) in the form

$$dV/dt = P/\omega, \tag{9}$$

where $dV/dt = Q$, the volume flowing past a fixed point in the tube in unit time. The viscous resistance is not a constant; at each value of l it is proportional to the area under the curve in Fig. 2 up to that point. If we determine this value of A_l for different values of l, a curve of A_l *vs.* l may be plotted as in Fig. 3. The value

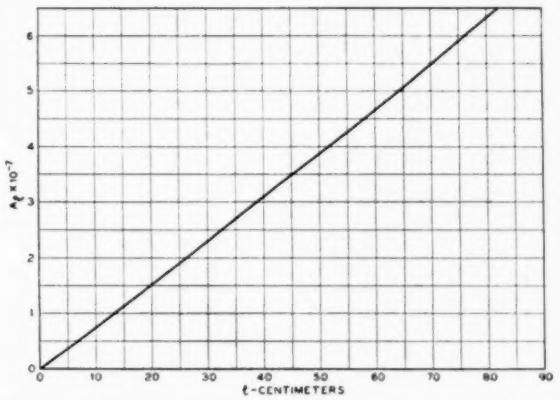

FIG. 3. Values of A_l determined from Fig. 2. This is not a straight line, as might at first appear.

of the viscous resistance is related to the ordinate of this curve by the relation:

$$\omega = (8\eta/\pi)A_l,$$

which gives the following upon substitution into Eq. (9):

$$dV/dt = \pi P/8\eta A_l.$$

* For the case of a uniform capillary, it is readily shown that the penetration is governed by the following relation: $l^2 = PR^2t/4\eta$. If l^2 is plotted against $PR^2t/4$ a straight line of slope $1/\eta$ will be obtained.

But $dV/dt = \pi R^2(dl/dt)$, whence

$$dl/dt = P/8\eta A_l R^2. \tag{10}$$

$A_l R^2$ is another function of l, represented, for example, in Fig. 4 and designated as $f_2(l)$ so that our differential equation finally becomes

$$f_2(l)dl = (P/8\eta)dt.$$

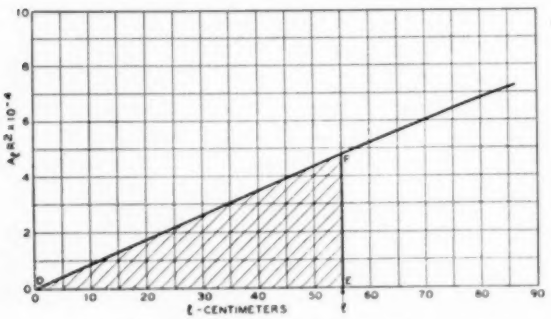

FIG. 4. $A_l R^2$ plotted as $f_2(l)$.

Referring to Fig. 4,

$$\int_0^l f_2(l)dl = \text{area } DEF.$$

If we call such areas B_l we may plot values of B_l *vs.* l as in Fig. 5, and hence B_l is designated as a third function of l, $f_3(l)$.

$$\int_{l=l_1}^{l=l} f_2(l)dl = f_3(l)\Big]_{l_1}^{l} = P(t-t_1)/8\eta.$$

The data obtained in using the plastometer consist of corresponding values of t and l. Values of $f_3(l)$ corresponding to the latter are taken from Fig. 5.

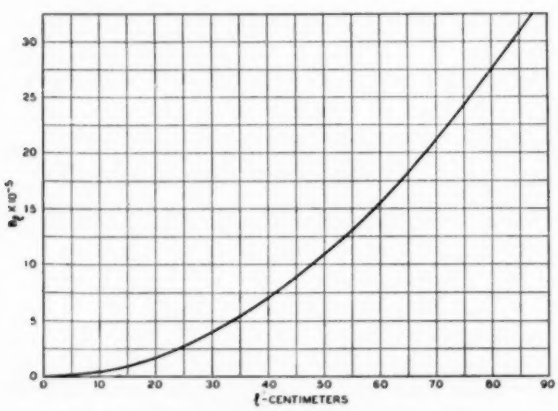

FIG. 5. Values of B_l determined from Fig. 4. B_l is designated as $f_3(l)$.

We now plot values of $f_3(l)$ as ordinates and t as abscissas; a straight line will be obtained (for a viscous material) of slope $P/8\eta$. If m is the slope determined from the experimental curve:

$$\eta = P/8m \tag{11}$$

or for any two corresponding values of t and l, we may simply use the equation,

$$\eta = P(t-t_1)/8[f_3(l) - f_3(l_1)].$$

APPLICATION TO DYNAMIC WETTING MEASUREMENTS

The application of this graphical method for which greatest use has been found in our laboratory is in studying the wetting of solids by liquids through investigating the rate of penetration of liquids into capillaries of solid material. The phenomenon of wetting is important in many technological fields, and our studies of degree of wetting have been materially assisted by the methods of analysis described herein.

If a liquid is brought into contact with a capillary opening, it will tend to penetrate into the opening with a force dependent upon the mutual attraction between the liquid and the solid wall. We shall call this force the "penetration tension," γ, which will be equal to $\lambda \cos\theta$, λ being the surface tension and θ the angle of contact between the solid and liquid surfaces under the conditions of measurement. The evaluation of γ is important in studies of wetting, and corresponds to the Freundlich[4] "adhesion tension" for values of θ greater than zero. For a liquid whose viscosity is known, γ can be calculated from observations on the advancing liquid in a capillary tube. A diagram of the apparatus used in this laboratory for studying wetting is shown in Fig. 6. Liquid is poured into A until it reaches a height in B just even with the capillary opening. As it moves into the capillary, the time is read at which the meniscus reaches each of the graduations on a scale placed behind the tube.* The

[4] Freundlich, *Colloid and Capillary Chemistry*, p. 157 (1926).

* It is easily demonstrated that for a cylindrical tube of uniform radius, the following relation holds: $l^2 = (R\gamma/2\eta)t$. Therefore, if l^2 is plotted against $(R/2\eta)t$, a straight line should be obtained with a slope equal to γ. However

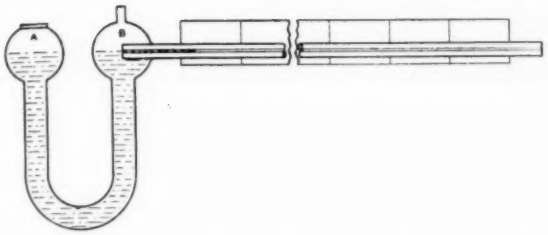

FIG. 6. Apparatus used to study wetting under dynamic conditions.

interior of the tube may be coated with a material the wetting of which is to be studied. This apparatus, which has proved useful in our studies of wetting, is similar to that used by Haller,[5] though the experimental procedure and the treatment of the data are entirely different.

The application of graphical calculation in this case is only slightly different and no more complex than the problem just treated above. As a matter of fact the procedure is identical up to Eq. (10), in which P will depend upon the penetration tension γ.

Since the force causing penetration is equal to $\lambda \cos\theta$ for each centimeter of periphery of the liquid-air interface,

$$P = 2\pi R\lambda \cos\theta/\pi R^2 = 2\gamma/R$$

so that we have

$$dl/dt = \gamma/4\eta A_l R^3. \qquad (12)$$

Now $A_l R^3$ is a function $f_4(l)$ as shown in Fig. 7. Eq. (12) takes on the form,

$$f_4(l)dl = (\gamma/4\eta)dt,$$

which gives upon integration

$$\int_0^l f_4(l)dl = \gamma t/4\eta \quad (t=0 \text{ when } l=0).$$

The integration of the left-hand member is performed by determining areas as above, the integral C_l being a function $f_5(l)$, as shown in Fig. 8.

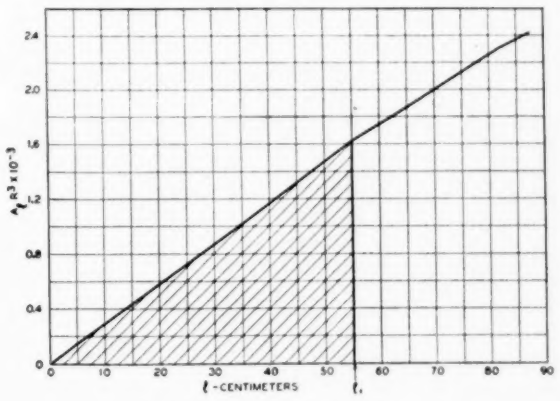

FIG. 7. $A_l R^3$ plotted as $f_4(l)$.

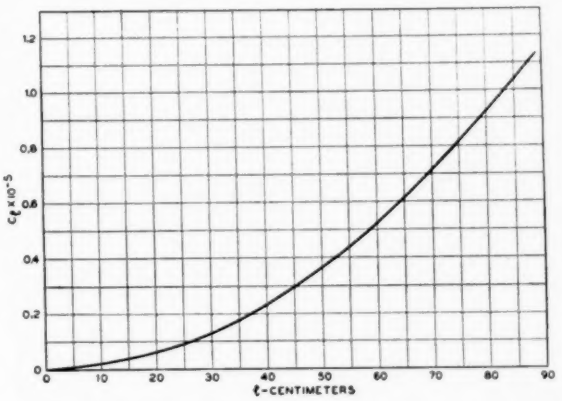

FIG. 8. Values of C_l determined from Fig. 7. $f_5(l)$.

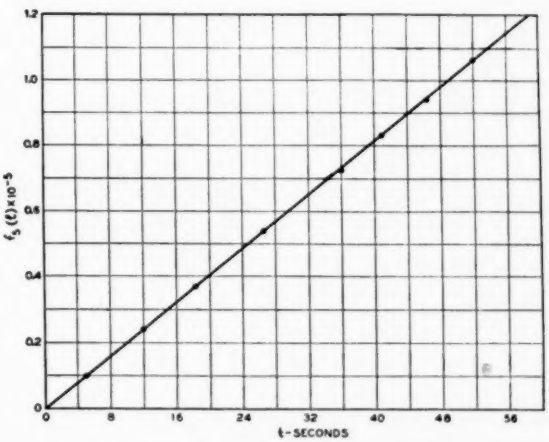

FIG. 9. Wetting of a glass capillary by water. γ(calculated from slope) = 70.2 dynes/cm.

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this procedure is not entirely satisfactory. It was difficult to find a tube with a uniform radius over great enough length to use in this work. Even after some care was taken in selecting a tube, reproducible variations from linearity in the plots of l^2 against $(R/2\eta)t$ could be traced to non-uniformity of bore.

[5] Haller, Kolloid Zeits. **54**, 7 (1931).

Since

$$f_5(l) = \gamma t/4\eta \tag{13}$$

we may plot values of $f_5(l)$ taken from Fig. 8 for various values of l against corresponding values of t from the experimental data. A straight line is obtained from which (η being known) the penetration tension γ may be determined. In Fig. 9 such a set of data is plotted for the penetration of water into the tube from which data were obtained to illustrate this paper.

The data were taken after the inner wall of the capillary had been thoroughly cleaned and then wet with water. (A line of much lower slope is obtained when a dry capillary is used, in agreement with the low value of γ observed by other investigators for water against dry glass.) From Fig. 9, the slope may be calculated as 2032, which is equated to $\gamma/4\eta$. At the temperature of test, $\eta = 0.00863$ poise, so that $\gamma = 70.2$ dynes per cm. It may be noted that this value agrees exactly with that obtained by Washburn,[6] in a paper proposing a similar method for measuring surface tensions.

[6] E. W. Washburn, Phys. Rev. **17**, 273 (1921).

The Balance-Plastometer; a Simple Instrument for Measuring Plasticity and Recovery of Soft Materials

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(Received January 4, 1933)

THE theory of parallel-plate plastometry has recently been studied extensively by Scott[1] and by Peek.[2] Though the time-flow relations for substances following Bingham's or de Waele's laws are more or less mathematically solved by these authors, this is not the case for substances like rubber, which have no true yield value. Peek says about rubber, that there occurs an "overlapping of the elastic and the plastic stage," so that the results are ambiguous.

This remark seems to us very much to the point. By reason of this "overlapping" the question of the "recovery" of masticated rubber and related substances is as yet rather unsolved. E. Karrer's[3] method of expressing plasticity ("softness") and recovery in one figure is not to be regarded as a solution of the problem. Moreover, his instrument for measuring the recovery has the great disadvantage of fixed time and rate of compression. There is no possibility of varying the time and the percentage of compression to any great extent; therefore, with his instrument it is not possible to study the way in which the "yield value" or the degree of plasticity varies with the time and the percentage of compression.

The instrument, described below, makes these variations possible and is simple of construction. The principle of this instrument is as follows: a bar is fixed to the long arm of a balance with unequal arms; the vertical displacement of this bar, which rests on a specimen of the material to be investigated, is magnified fifty times and read on a scale. The specimen rests on a second bar with a known cross section. The first named bar can be loaded with a known weight, and this weight can be removed at will.

Figs. 1, 2 and 3 give top view, front view and some details respectively. In Fig. 4 a photograph of the apparatus as used by the author is shown.

The specimen is pressed between the two bars d and e (see Figs. 2 and 3) which have flattened ends. The lower bar e is fastened to the ground plate by means of a spring clamp, which allows an easy detaching and reinstalling of this bar. This clamp is shown in front view A (see Fig. 2) and in side view L and M (see Fig. 3). The bar e normally has a round upper surface of 1 cm²; the upper part of this bar can be unscrewed and replaced by similar parts of a surface of any size wanted. The under surface of the upper bar d is about 2 cm². In this way, the modification of the Williams plastometer[4] by van Rossem[5] is put into practice: the pressure on the specimen is kept constant and volume control of the specimen is eliminated. The latter point is of great practical importance.

The upper bar d is fastened to the long arm of the balance b (see Figs. 2 and 3). The bearings of this balance are at o. In detail Q (Fig. 2) one of these bearings with the steel ball which bears the balance-yoke, is shown. While at one bearing (o_1, Fig. 1) this ball rests in a flat slit in its bearing-support, at the other bearing (o_2, Fig. 1) this ball rests in a conical hole in the corresponding support, thus giving scope for little differences in thermal expansion of yoke b and basal plate a (see Fig. 1).

A sharp pin (see Fig. 2, detail P) rests in a little hole at the top of the upper bar d; this pin transmits the displacement of this bar to a needle n (see detail O, Fig. 2). A little steel spring (see q, Fig. 2) gives the necessary pressure on the needle from both sides.

The fulcrum axis of this needle and its sup-

[1] J. R. Scott, Tr. I. R. I. **7**, 169–186 (1931–1932).

[2] R. L. Peek, Jr., J. Rheology **3**, 345–372 (1932).

[3] E. Karrer, Ind. Eng. Chem. An. Ed. **1**, 158–159 (1929).

[4] Compare O. de Vries, Archief v. de Rubbercultuur **9**, 260 (1925).

[5] A. v. Rossem and H. v. d. Meyden, Kautschuk **3**, 369 (1927); *India R. J.* **76**, 360–363 (1928).

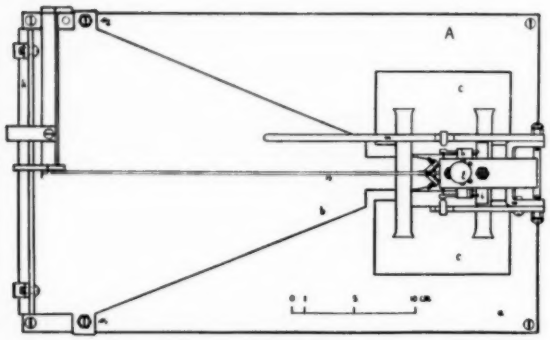

FIG. 1. Top-view of plastometer.

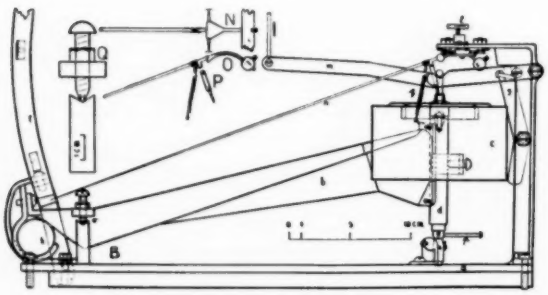

FIG. 2. Front-view of plastometer.

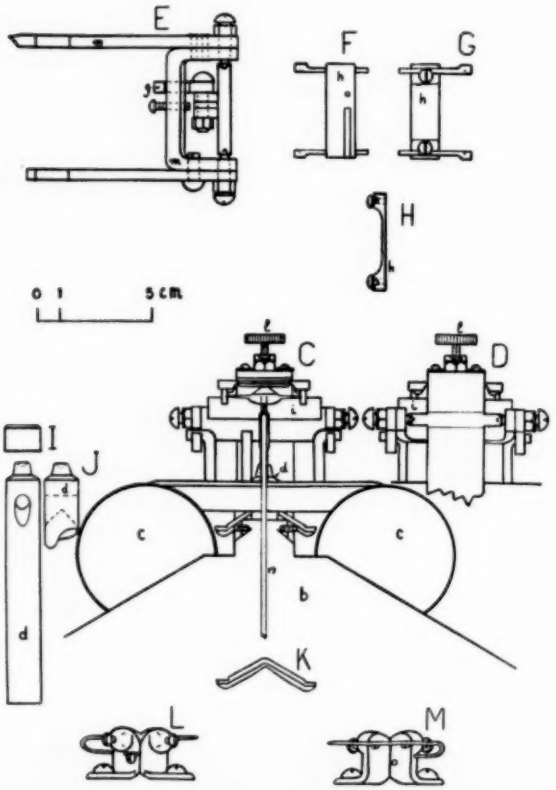

FIG. 3. Details of plastometer.

ports are shown in position in Fig. 2 and separately: in top view at Fig. 3 *F*; from underneath at Fig. 3 *G*; and in side view at Fig. 3 *H*. The screw *b* (Figs. 1, 2 and Fig. 3 *C* and *D*) allows for zero adjustment. By this gauge the thickness of the specimen is read on the scale with an accuracy of 0.0003 cm.

Needle *n* and balance *b* are both counterbalanced by weights *i* and *k* respectively (see Fig. 2). The total friction amounts to 5 grams at maximum. In this way not more than a force of 5 grams is exerted on the specimen, when

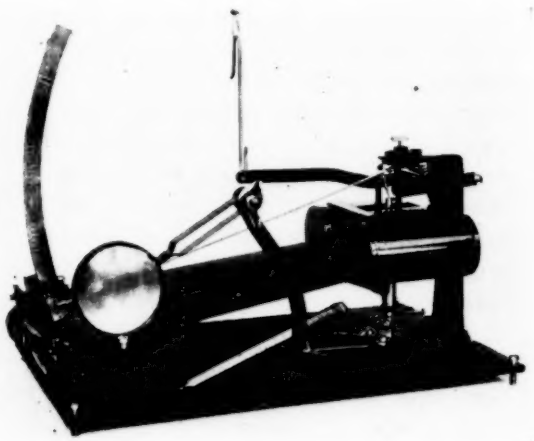

FIG. 4. The balance-plastometer.

the pressing weight is arrested. The upper bar *d* may be loaded and unloaded with a weight *o* of 5 kg made up of two iron bars which hang in the unloaded position on the yoke *m*. This yoke can be operated from outside the air thermostat, in which the whole apparatus is placed during use. In the loaded position (brought about by the lowering of the yoke *m*) this weight rests on a little steel yoke (shown in full at Fig. 3 *K* and in position at Fig. 3 *C* and Fig. 2). This latter yoke transmits the force of 5 kg to the center of the upper bar *d* (Figs. 3 *I* and *J*), thus preventing rotation momentums working on this bar.

It is thought, that the slight nonparallel motion of the under surface of the upper bar against the upper surface of the lower bar is of no influence on the readings of the instrument as compared with the readings of a true parallel-plate plastometer. This supposition is proved by the comparison of plasticity measurements of

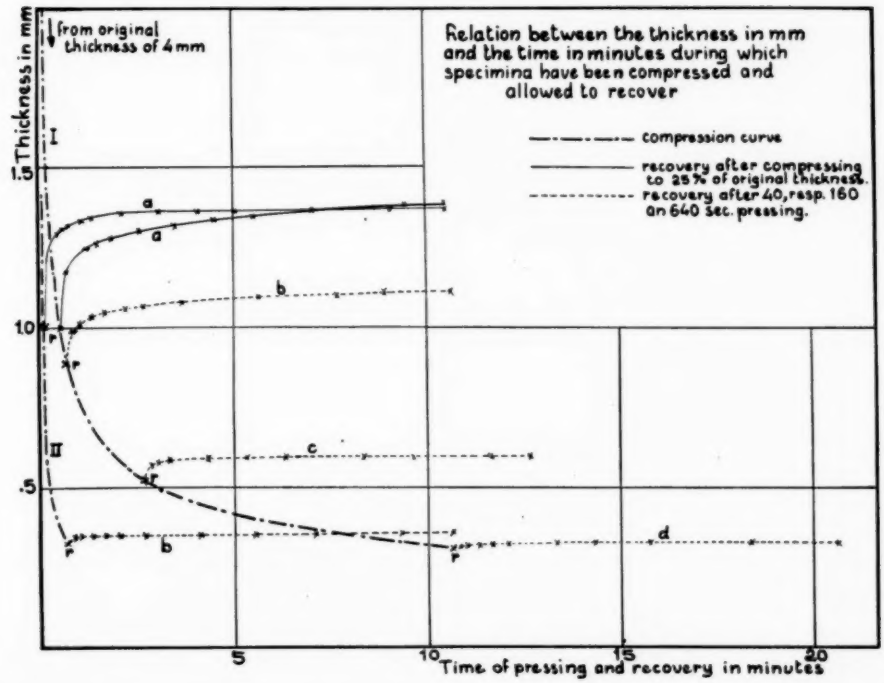

FIG. 5. Recovery measurements on two stocks of masticated rubber: (I) masticated for 8 minutes; (II) masticated for 50 minutes. Curves *a*. Recovery measured after compression by 5 kg/cm² from an initial thickness of 4 mm to a final thickness of 1 mm. Curves *b*. Recovery measured after compression for 40 seconds. Curve *c*. The same after compression for 160 seconds. Curve *d*. The same after compression for 640 seconds. At the point *r* the weight was lifted and recovery began.

the same masticated rubbers by this instrument and by the modified Williams plastometer of the Netherland Government Rubber Institute (see Table I).

TABLE I. *"Plasticity" or "softness" measurements with the balance plastometer and with the modified Williams plastometer of the Netherland Government Rubber Institute (both with 5 kg/cm² at 70°C).*

Material		Balance pl.	N.G.R.I. pl.
F.L. Sheet masticated 5 min.	D10	0.360*	0.364
		0.350	0.385
	D30	0.242	0.238
		0.230	0.250
F.L. Sheet masticated 10 min.	D10	0.263	0.291
		0.261	0.294
	D30	0.166	0.176
		0.170	0.178

* Before measuring the plasticity with the balance plastometer, the initial thickness of the specimen is brought to 4±0.05 mm, by compressing and unloading the specimen in the apparatus, till it recovers to the thickness named. This measure, which is unpracticable with the Williams-type plastometer, gives better reproducibility for plasticity-data of stiffer rubbers.

Several ways of measuring the recovery could be proposed. Any duration of time of pressing could be chosen and recovery measured after tilting the weight for any other length of time. It is also possible to compress the specimen to a certain percentage of its original thickness, in which case the time of compressing will vary with the plasticity of the material under examination. In Fig. 5 some examples are given of both methods of measuring the recovery, obtained on two stocks of sheet, masticated for 8 and 50 minutes respectively on laboratory mills. These examples are only meant to illustrate the two ways of measuring the recovery and the functioning of the instrument.

The following considerations indicate, that measuring the recovery after compressing to a certain percentage of the original thickness might prove advantageous.

If an "elastico-plastic" (Peek[2]) material be put under strain, the inner elastic stresses

caused by this strain will diminish slowly because of the inner flow originating from these same stresses.[6] To measure the elasticity of an elastico-plastic substance, it is best to study the initial inner stresses, occurring in a strained body of this substance, regarding the influence of time on these stresses as a rheïc phenomenon. If it proves impossible to measure these stresses immediately, one should take precautions to have these stresses always influenced to the same extent before the measurement is finished. Now if we let the inner flow, which tends to diminish to inner stresses, work for a time adapted to the plasticity of the material in such a way that the total flow is equal in each case, this condition will be fulfilled. This is done by compressing the material from a certain initial standard thickness to a final standard thickness.

In conclusion it may be said that the instrument offers advantages when used to measure the plasticity as well as when used to study the recovery.

In the first case, the same way of measuring the plasticity is used and the same precautions as to temperature of apparatus and specimen are taken as described by van Rossem[5] for the N.G.R.I. plastometer. Advantages of the above-described instrument are: (1) Control of initiai thickness as described in starred reference to Table I. (2) Thickness is measured with greater accuracy.

In the second case, several ways of measuring the recovery are practical. The method used by the author is as follows: a cylindrical specimen, 17 mm in diameter and 5 to 8 mm in thickness is placed in the thermostat (usually at 70°C) for at least 10 minutes. After this time the pellet is placed between the bars *d* and *e* and temperature equilibrium in the stove is restored by means of an electric fan with resistance coil, both of which are placed in the stove. This done, the thickness of the specimen is brought to 4 mm$\pm$0.05 mm, in the way described in starred reference to Table I. Then the weight of 5 kg is lowered quickly and the specimen is compressed. As soon as a thickness of 1 mm is attained the weight is lifted and simultaneously a stopwatch is started. Readings are now taken at fixed times up to 10 minutes.

The compression, being here 75 percent, may be varied, so that the whole range of compression of from zero to 100 percent may be studied. This is thought to be advantageous in studying such problems as the influence of time of stressing on the yield value of rubber.

[6] E. Bingham, J. Franklin Inst. **197**, 99–113 (1924).

On the Turbulence Statistics in Burgers' Phase Space

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IT is well known that turbulent flow is of fundamental importance in hydrodynamics. In turbulent flow the streamline pattern changes from instant to instant, and the instantaneous velocity at any point fluctuates quite irregularly in magnitude and direction about its mean value, for which, up to the present time, it has been possible to derive only more or less empirical laws. It is appropriate, therefore, to attack such irregular fluid motion by the methods of statistical mechanics. A notable beginning in this direction was first made by Th. von Kármán[1] in 1924. Several years later, J. M. Burgers[2] accomplished a significant methodical advance in this direction, by constructing for certain simple cases of turbulent motion, a phase space, in which the analogy with the Liouville theorem of classical statistical mechanics holds.

Burgers treats the flow between two parallel walls, where the x-axis is chosen parallel to the walls, and the y-axis normal to the walls. The extent of the fluid in the z-direction, normal to x and y, is assumed great, so that the assumption of two dimensional flow made in the following analysis is justified in a sense. The flow can then be fully characterized by a stream function ψ, which depends on x, y, and the time t. The consideration is further limited to a finite length of the channel in the x direction. The magnitude of this length is taken much greater than that of the channel breadth.

Burgers now applies an ingenious simplifying device, by replacing the continuous x, y-coordinate field by a quadratic point lattice, in which the spacing of the lattice points, or "mesh width" ϵ, is assumed very small compared with the channel breadth. Then, the state of flow at any instant can be characterized with sufficient accuracy by a finite number of quantities, namely the values of the stream function at the finite number of lattice points. The velocity components are given in the continuous x, y-coordinate field by differential quotients of ψ with respect to y and x respectively, and must therefore be represented in the point lattice by certain difference quotients.

Burgers now takes the values of the stream function at the lattice points as coordinates of his phase space. Each instantaneous state of flow is completely given, therefore, by a point in this polydimensional space. He succeeded in proving the validity of the Liouville theorem for this phase space under the assumption of ideal, incompressible and frictionless flow, whereby, by known methods, a basis for the calculation of the most probable distribution of ψ is given. As a subsidiary condition, Burgers uses in place of the energy condition of classical statistical mechanics, the so-called dissipation condition, which determines the equilibrium of the energy transmitted to the fluctuations from the mean motion, with the energy dissipated by the viscosity. Unfortunately, however, the calculations prove to be very difficult, so that Burgers is obliged to make very rough approximations, and his results concerning the mean velocity distribution, etc., are of very limited value.

The present writer undertook the task of obtaining, at first, mathematically correct results by making use of the Burgers' phase space. For the development of analytical methods, at first the usual energy condition was taken as the subsidiary condition. To be sure this cannot be sufficient for a complete turbulence statistics, but, nevertheless, gave very useful information. Using the energy condition, we have to postulate a given value of

$$\sum \psi_x^2 + \psi_y^2,$$

where the summation is to be taken over all lattice points of the considered portion of the

[1] Th. von Kármán, Proc. 1st. Intern. Congress for Applied Mechanics, Delft, 1924, p. 97.

[2] J. M. Burgers, Proc. Koninkl. Akad. van Wetensch. te Amsterdam **32**, 414, 643, 818 (1929).

channel. For ψ_x and ψ_y the "forward difference quotients" may be taken in such a way that, for instance, at the lattice points with the original coordinates x_0, y_0, we have:

$$\psi_x = [\psi(x_0+\epsilon, y_0) - \psi(x_0, y_0)]/\epsilon,$$

$$\psi_y = [\psi(x_0, y_0+\epsilon) - \psi(x_0, y_0)]/\epsilon.$$

It was possible to carry out the discussion of this statistics rigorously. The most striking result was obtained when the calculation of the mean value of the product $\psi_x\psi_y$ was undertaken, say, for the center of the channel. First we took, as above, the forward difference quotients for ψ_x and ψ_y; secondly, however, we used for ψ_x and ψ_y the "central difference quotients," so that, for the lattice point with the coordinates x_0, y_0 we could set

$$\psi_x = [\psi(x_0+\epsilon, y_0) - \psi(x_0-\epsilon, y_0)]/2\epsilon,$$

$$\psi_y = [\psi(x_0, y_0+\epsilon) - \psi(x_0, y_0-\epsilon)]/2\epsilon.$$

When we now calculated the mean value of the above-mentioned product with the help of the central difference quotients, we obtained as expected the value zero. On the other hand, by making use of the forward difference quotients we obtained a finite value, which did not vanish even when the lattice spacing, ϵ, was decreased to zero by applying a limiting process to the results. This paradoxical result, which is wholly unacceptable, gives evidence, in conjunction with other facts, that the velocity fluctuations with wave-lengths of the order of magnitude of the lattice spacing ϵ, preponderate to an unallowable degree. This behavior is roughly more analogous to that of a crystal rather than to that of a fluid. Evidently, by the artificial introduction of the point lattice, a discontinuous element wholly foreign to the continuous fluid was introduced into the considerations.

A proposal for overcoming this essential difficulty was made in the detailed report of this work which was sent in October, 1932, to the Editor of the *Zeitschrift für angewandte Mathematik und Mechanik*. In this paper the dissipation condition was abandoned as the subsidiary relation required in the setting up of the turbulence statistics problem. This was done essentially for two reasons. First the use of the dissipation condition implies that viscosity plays a determining rôle, while experiment indicates a negligible influence of viscosity in the greater part of the fluid. Second, the proof of the fundamental Liouville theorem rests upon the assumption of an ideal fluid for which there can be no dissipation. The elimination of the dissipation required a detailed discussion of possible alternative subsidiary conditions. The condition finally adopted was closely connected with the shearing stress at the wall which, because of the condition of equilibrium with the pressure drop, determines the shearing stress distribution in the entire fluid region. This assumption has received support from the recent experiments carried out at the California Institute of Technology by A. M. Kuethe and F. L. Wattendorf which have clearly demonstrated the essential importance of the shearing stress distribution in determining the statistical behavior of the velocity fluctuations. The results of our calculations are, however, physically not yet satisfactory, which may be perhaps explained by the fact that the actual turbulence is probably three dimensional, even when the mean motion is two dimensional.